Electrochimica Acta 130 (2014) 551–558

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Enhanced Electrochemical Performance of Maghemite/Graphene Nanosheets Composite as Electrode in Half and Full Li–Ion Cells

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A R T I C L E I N F O

Article history:
Received 30 August 2013
Received in revised form 20 January 2014
Accepted 1 March 2014
Available online 15 March 2014

Keywords:
Li-ion battery
Anode material
Graphene composite
Maghemite
Full Cell

A B S T R A C T

A composite consisting of iron oxide/graphene nanosheets (GNS) is synthesized by hydrothermal treatment of a mixture of graphitic oxide and $FeCl_2$ in the presence of N_2H_4 as reducing agent. Special attention is given to the characterization of the iron oxide owing to the disparity of criteria found in literature to distinguish between maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4). Here, the oxide is accurately characterized as γ-Fe_2O_3. The beneficial effect of the simultaneous formation of GNS and γ-Fe_2O_3 is reflected in the capacity of the cell, which is much higher than those of the individual components. This may be the result of a synergistic effect of the good conducting properties of graphene, its buffering action on the volume changes undergone by γ-Fe_2O_3 on reacting with Li and the high capacity of this oxide. The composite also has good rate capability and can recover its capacity at low current intensities after prolonged cycling at high rates. The composite performs very well in a full cell configuration with $LiFePO_4$ as cathode, where it exhibits an average discharge capacity of 122 mAh g^{-1} and excellent capacity retention over 50 cycles. In addition, the cell has good rate capability at current densities as high as 5C.

1. Introduction

Although most commercial Li-ion batteries use graphite as anode, a variety of materials have been investigated in order to increase the cell capacity, and therefore its specific energy. Some of these materials are transition metal oxides, which are able to store more Li per gram than graphite, thus giving rise to higher specific capacities. Special attention in this respect has been given to Fe, Co and Ni based oxides [1–4]. Ni and especially Co are expensive and toxic, so the practical interest of the former element is questionable while iron oxides are not subject to these problems, [5] so they may be effective alternatives. An important drawback of their cycling behavior is the volume changes undergone upon discharging and charging that results in the disintegration and disconnection of the active material from the current collector, which is the origin of the capacity fading [6,7].

This shortcoming is very often circumvented by using carbon-based composites. In addition to buffering expansions and shrinkages, carbon has conductive properties that enhance the mobility of the charge carriers. In the last few years, graphene has become one of the most widely studied materials for Li-ion battery electrodes. Interest in this material has been aroused by two outstanding properties, namely: its high specific capacity (744 mAh g^{-1}, which is twice that of graphite) and its high electronic conductivity, up to 10^2 S m^{-1} for GNS, depending on the preparation method used [8]. In fact, graphene has been the subject of much research intended to improve the performance of these electrochemical devices [9]. GNS have also been used as additives to improve the performance of other electrochemically active materials (particularly tin, nickel and cobalt oxides) [10].

Magnetite (Fe_3O_4) is the most widely iron oxide studied in composites with GNS as anode for Li-ion batteries. Unfortunately, the electrochemical response of Fe_3O_4/GNS composites differs widely as regards to performance in Li cells. For example, while Behera [11] obtained specific capacities, after 100 cycles, as high as 1200 mAh g^{-1} at a rate of 2000 mA g^{-1}–really very high for this type electrode–, Lian *et al.* [6] with current density of 50 mA g^{-1}, and Huang *et al.* [12] at a rate of 500 mA g^{-1}, obtained capacity values of 50% of that at the 40th cycle. Hematite (α-Fe_2O_3) has also been studied but at a lower extent and with similar performances as magnetite [13–15]. There is little information on the electrochemical performance of maghemite (γ-Fe_2O_3) as anode material, and even less in GNS composites. We only know a single article on this composite recently published [16]. This contrasts with the abundant literature available for magnetite [6,7,11,12,17–24] and hematite [13–15] based composites. The confusion between

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http://dx.doi.org/10.1016/j.electacta.2014.03.037

magnetite and maghemite might be one of the reasons of this circumstance.

Besides the absence of studies on maghemite/GNS composites, there is the problem of the lack of an accurate knowledge of the actual nature of the iron oxide. So far, most of reports on iron oxide/GNS composites have assumed the magnetite to be the iron oxide phase present in the composite, occasionally on the grounds of an arguable interpretation of the characterization results. Magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are two structurally related phases that are difficult to differentiate by X-ray diffraction and Raman spectroscopy, which are commonly used to characterize these composites [7,12,17–24]. We accurately identified the phase formed as γ-Fe_2O_3 rather than Fe_3O_4 in spite of the experimental conditions used in the composite synthesis.

As stated above, most studies on the electrochemical properties of graphene based composites in Li batteries have been carried out in half cells (versus a Li metal electrode). In fact, very few papers have addressed their use in full Li-ion batteries [22,25]. In this work, we examined Li storage properties in a full cell configuration using $LiFePO_4$ (LFPO) as cathode. The outstanding performance of this composite in both half and full cells opens promising prospects for a new generation of Li-ion batteries exploiting the synergistic effects of the electrochemical properties of the two components, which lead to improved reversible Li storage.

2. Experimental

2.1. Materials

Iron oxide–graphene nanosheets composites (MG) were prepared by a hydrothermal method. In a typical run, 1.23 g of $FeCl_2{\cdot}4H_2O$ was mixed with 0.2 g of graphene oxide (GO) synthesized as described elsewhere [26] in 100 mL of water for 2 h in order to bring particles into intimate contact. Then, 2 mL of the reducing agent ($N_2H_4{\cdot}H_2O$) was added and mixed for 10 min. Next, the whole mixture was transferred into a 135 mL autoclave where the mixture was allowed to react at 150 °C for 14 h. The product thus formed was filtered and washed several times with water to neutral pH and dried at 80 °C. In order to compare the performance of the individual materials, graphene nanosheets (GNS) and iron oxide (MH) were prepared separately, using the same procedure as with the composite. The cathode of the full cell configuration was made from commercial $LiFePO_4$ supplied by Phostech Lithium Inc., with a 2.1% carbon coating and used as received.

2.2. Samples Characterization

XRD patterns were recorded on a Siemens D5000 X-ray diffractometer using non-monochromated Cu Kα radiation and a graphite monochromator for the diffracted beam. The scanning conditions for structural analysis were 5–90° (2θ), a 0.03° step size and 12 s per step. Thermogravimetric measurements were made under ambient conditions, using a TGA/DSC 1 thermobalance (Mettler Toledo) at a heating rate of 5 °C min^{-1}. TEM images were obtained with a Philips CM-10 microscope operating at 100 keV. Raman measurements were made with a Renishaw inVia Microscope equipped with a Renishaw CCD Camera detector (578 × 400) and a laser of 532 nm edge in the Linefocus mode. XPS recordings were obtained on a Physical Electronics PHI 5700 spectrometer, using non-monochromatic Mg Kα radiation and a multichannel detector. All spectra were fitted to Gauss–Lorentz curves in order to better identify the different chemical environment in each material.

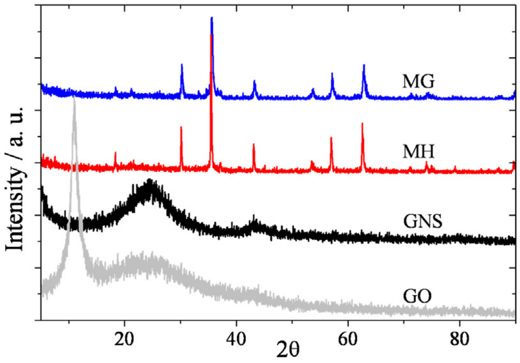

Fig. 1. XRD pattern for graphene oxide (GO), bare graphene nanosheets (GNS), pure iron oxide (MH) and composite (MG).

2.3. Electrochemical Measurements

The electrodes were prepared by mixing the active material with PVDF (Fluka) and carbon super P (Timcal) [weight proportion of 80:15:5 (for GNS and composite) and of 80:10:10 (for $LiFePO_4$)] and adding 1-methyl-2-pyrrolidinone (Sigma-Aldrich) to obtain a slurry for coating the electrode material on a Cu foil, using the “doctor-blade” technique. The coated electrodes were pressed at 1.5 ton cm^{-2}. In order to know the electrochemical behavior of the composite, the individual components and $LiFePO_4$ we have studied their performance in half-cells with Li foil as counter electrode. These measurements were carried out in CR2032 coin cells (electrodes made from the composite and its individual components) and Swagelok type cells (electrode made from $LiFePO_4$). The electrolyte was 1 M LiBOB (Novolyte) dissolved in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC). Cycling tests for GNS, MH and composite MG were performed within the potential window 0.01–3.0 V. For $LiFePO_4$ the potential window was 2.5–3.9 V. All these measurements were carried out on an Arbin BT2000 potentiostat–galvanostat system, using the following current densities: 100 and 1000 mA g^{-1} for the composite and its individual components, and 34 mA g^{-1} for $LiFePO_4$. The rate capability of the composite was measured raising the current density of the half-cell from 100 to 200, then to 1000 and finally, again, 100 mA g^{-1}, with cycling at each current density for 10 and 30 cycles. The performance of the composite as anode material in a full cell configuration was assessed by assembling a Swagelok type cell with $LiFePO_4$ as cathode and the same electrolyte used in the half cell configuration. Before the full cell was assembled, the anode was placed in contact under pressure with Li foil soaked in LiBOB electrolyte for 5 min. The full cell was assembled with a cathode to anode mass ratio of 2.2 (0.6 and 0.3 mg cm^{-2}, respectively). For comparison, similar cells were assembled with MH, both pristine and prelithiated, and pristine MG. The full cells were galvanostatically cycled at 34 mA g^{-1} (C/5 referred to $LiFePO_4$ being C = 170 mAh g^{-1}) from 1.5 to 3.9 V over 50 cycles. The rate capability of the full cell was also evaluated over 10 cycles each at 1 C, 2 C and 5 C, and 20 cycles at 2 C. Moreover, other cathode to anode mass ratio (4.1) was tested, this one corresponding to a cathode to anode average capacities close to 1, which is the ideal ratio

3. Results and Discussion

3.1. Structural, Chemical and Morphological Characterization

Fig. 1 shows the X ray diffraction patterns for the samples studied. Exfoliation and reduction of GO in the solvothermal treatment was revealed by the complete absence of the peak at 10.3° and the presence of the characteristic peak for graphite at *ca.* 26.4° [26]. Its